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13. ABSTRACT (Maximum 200 Words) The primary goal of this research has been the development of a new helium droplet spectrometer, based upon the use of a PPLN-OPO laser. Although the laser is commercially available, considerable development was required to make the system tunable. We have succeeded in this effort and the laser is now being used to carry out a range of studies related to our AFOSR funded research project dealing with the formation of highly reactive radical nano-solids. The high output power of this laser system, combined with its wide tunability, great enhance the capabilities we have in our laboratory. In parallel with the laser developments, we have built up a new helium droplet apparatus, which is also now fully functional.					
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Superfluid Helium Droplet Spectroscopy Equipment Development

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Final Report

Objectives

The primary goal of this research has been the development of a new helium droplet spectrometer, based upon the use of a PPLN-OPO laser. Although the laser is commercially available, considerable development was required to make the system tunable. We have succeeded in this effort and the laser is now being used to carry out a range of studies related to our AFOSR funded research project dealing with the formation of highly reactive radical nano-solids. The high output power of this laser system, combined with its wide tunability, greatly enhance the capabilities we have in our laboratory. In parallel with the laser developments, we have built up a new helium droplet apparatus, which is also now fully functional. The ultimate goal of these studies remains the stabilization and study of a whole new class of free radical nanosolids, resulting from the unique cluster growth conditions in helium nanodroplets. The spectroscopic methods used in these studies are now well developed. In parallel with these experiments on free radicals, studies have been performed on hydrogen clusters, the goal being to understand how effective these systems are as isolation media. These studies have revealed that, even at the low temperature of the helium droplets (0.37 K), the hydrogen molecules are quite mobile, resulting in a single isomer for each cluster size. This has important implications concerning the prospects for isolating reactive species in hydrogen clusters.

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Small molecular and atomic free radicals (O, H, OH, CN and NH_2) play a key role in many important atmospheric¹ and combustion² reaction mechanisms and their properties have thus been the subject of intense research. In particular, there is a rich literature dealing with the deposition and creation of reactive species in cryogenic solid matrices,³⁻⁶ including stable and transient complexes with oxygen atoms and ozone⁷⁻¹² and rare gas complexes with OH^{13,14} and CN^{15,16}. In view of the high reactivity of the free radicals, it is not surprising to find that in most cases the radicals are only present in low (trace) quantities. The stability of the solid is dependent upon the slow diffusion rate of the radicals through the matrix at low temperatures. Low radical concentrations translate into low energy densities for these solids, focusing the quest for higher energy materials of this type around finding ways to increase the concentration of radicals in the solid, while at the same time stabilizing them so that they do not react spontaneously.

The research proposed here takes advantage of methods recently implemented and developed in our laboratory to explore an entirely new approach for producing high radical densities in nanosolids. The goal is to completely eliminate (or at least dramatically reduce) the need for the inert matrix material used in the matrix isolation studies discussed above. The idea is to make use of the highly structured nature of long-range intermolecular interactions in order to help stabilize the radical solids, without the need for separating them using molecular spacers. The approach is to grow the nanosolids in liquid helium, such that the energy of the radicals is sufficiently low that they cannot react, because of the barriers that lie between the van der Waals minima on the surface and the much deeper chemical well at short range.

Status of Effort

The experimental apparatus built up over the past two years is shown in Figure 1. The PPLN-OPO laser is directed along the helium droplet beam in order to optimize the laser induced depletion signals. This is possible because the quadrupole is operated off axis. In several cases we are able to deplete a large fraction (0.8) of the droplet beam, owing to the high power of the laser.

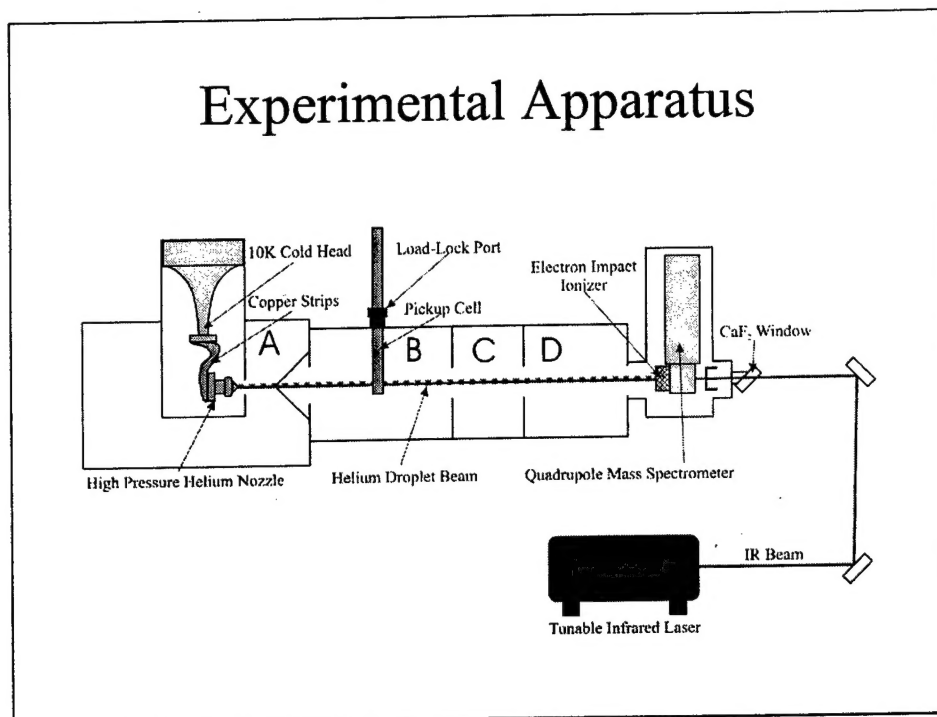


Figure 1: Experimental apparatus.

The research carried out in the previous grant period has already lead to the publication of several papers^{17,18,19}. In addition, we have a large amount of data that is currently being analyzed and will be published in the coming year.

The developments we have made in the tuning of the laser are being incorporated into the commercial system and should make this laser more user friendly for others purchasing it in the future.

Accomplishments and New Findings

Figure 2 shows a Stark spectrum of the propargyl radical, recorded with an F-center laser, along with the corresponding fit. This spectrum was used to obtain the first experimental value for the dipole moment of propargyl, namely 0.15 D^{44} . With the pyrolysis source at high temperature, the precursor molecule was almost completely dissociated.

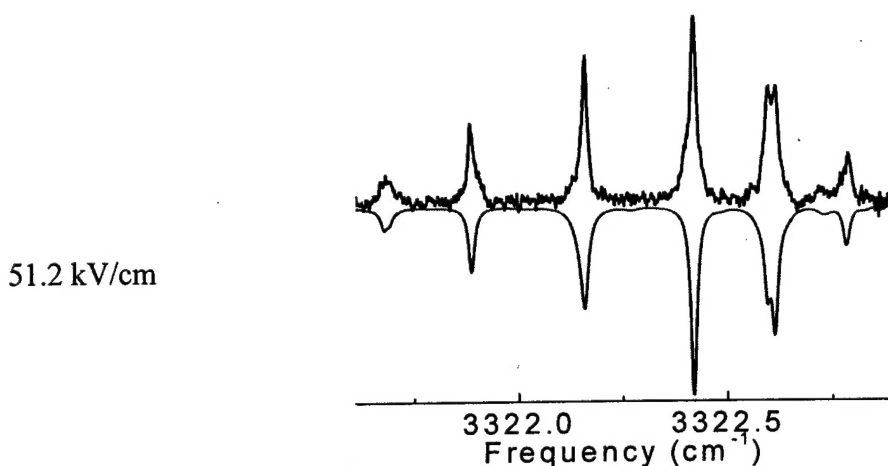


Figure 2: Stark spectrum of the C-H stretch of propargyl.

Infrared spectra have also been obtained for HCN and HF clusters with Cl, Br and I atoms. Figure 3 shows two pendular spectra (a large electric field is used to collapse the ro-vibrational spectra into a single peak ⁸), one with the bromine source at room temperature and the other with it heated to the point where molecular bromine is almost entirely dissociated. The new feature that appears at high temperature is easily assigned to the HF-Br complex,

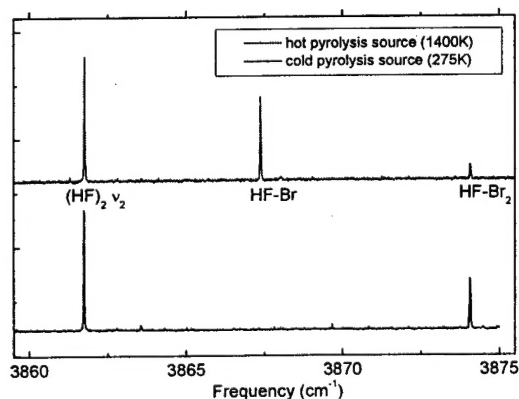


Figure 3: Pendular spectra showing the formation of Br-HF.

from the pickup cell pressure dependence of the signals and the zero field spectrum shown in Figure 3. The overall P,Q and R branch structure is obvious in these spectra

and the complete assignment and fitting is underway. The corresponding X-HCN complexes have also been studied and are currently being analyzed.

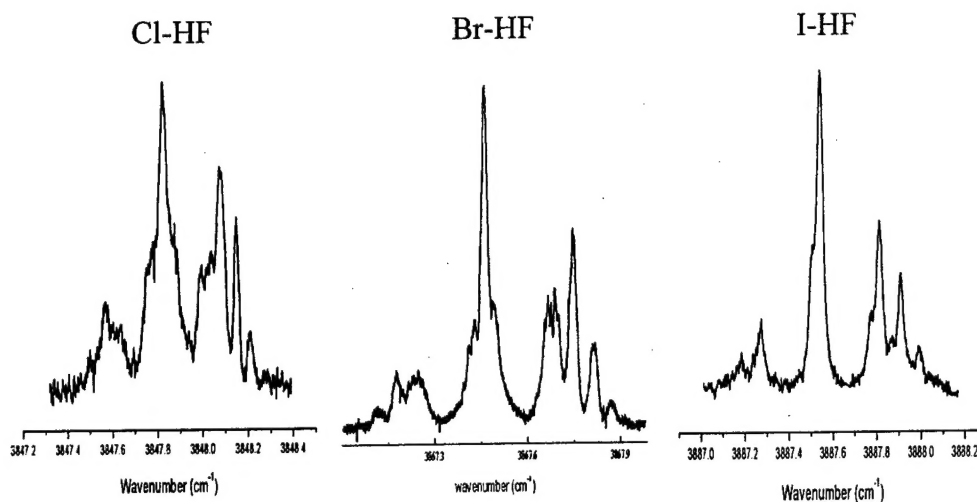


Figure 4: Infrared spectra of X-HF complexes.

Now that we have all of the capabilities necessary to make and study these radical complexes, we are in the position to move on to the more reactive systems discussed above, namely those containing multiple free radicals.

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AFOSR EQUIPMENT GRANT

"Superfluid Helium Droplet Spectroscopy Equipment Development"

Vendor	Item	Amount
CTI-Crogenics (Helix)	Coldhead, Compressor	5,592.56
Linos Photonics, Inc.	OS4000OPO	106,000.00
Linos Photonics, Inc.	Mephisto 2500 Pump Laser	59,000.00
New Focus	Optical Transport System	585.86
Boc Edwards	Edwards Pumping Station	6,821.58
	Total	178,000.00